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Project R-120 (Q5)

Electrochemical Destruction of Perfluorooctanesulfonate in Electroplating Wastewaters

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Summary

Work this past quarter focused on testing of the reactor that was developed in past quarters for electrochemical oxidation of poly- and per- fluoroalkyl substances (PFAS) using a tubular Magnéli phase titanium sub-oxide (Ti_4O_7) reactive electrochemical membrane (REM). The oxidation experiments were performed in synthetic solutions, using a crossflow setup in full recycle mode. The synthetic solutions were prepared by spiking perfluorooctanoic acid (PFOA) into a background electrolyte that has an ionic strength that is representative of industrial electroplating wastewaters (*i.e.*, 240 mM $NaClO_4$). The solution was subjected to electrochemical oxidation at a constant current density (30 mA/cm²) for between 5 to 9 hours, achieving > 90% PFAS removal.

The reaction rate constants were found to be approximately second-order with respect to total PFAS concentration, indicating that interactions between adsorbed intermediates is likely involved in the reaction mechanism. Additionally, shorter-chain PFASs were observed to form and degrade throughout the experiment. Therefore, future work will focus on improving electrocatalytic activity to minimize the production of these compounds.

Electrochemical oxidation experiments

The operating conditions for the electrochemical oxidation experiments are shown in Table 1 and results are shown in Fig. 1. Three initial PFAS concentrations were investigated (*i.e.*, 0.1, 1.0, and 10 μ M) to determine the effect of initial concentration on

Table 1 - Operating parameters of PFAS oxidation experiments.

Parameter	Value
[PFOA]	0.1 to 10 μ M
Electrolyte	240 mM $NaClO_4$
pH	6.2
Conductivity (mS/cm)	22
Flowrate (LMH)	828 \pm 2.1%
Current density (mA/cm ²)	30
Cross flowrate	46 \pm 13.04%
Duration	5-9 hours
Mode	100% recycle

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removal. It was found that rapid removal was observed for the initial two hours of the experiment (*i.e.*, > 80% removal) followed by a slow removal to > 90% over the duration of the experiment (Fig. 9a). All three concentrations showed the production of short chain compounds, which is in line with the literature. The concentrations of PFHpA, PFHxA, and PFPeA are shown in Fig. 9b for the 10 μM initial PFOA concentration and are produced at < 2.7% of initial PFOA. The trends for these short chain compounds indicate that they are both being produced and degraded during the experiment.

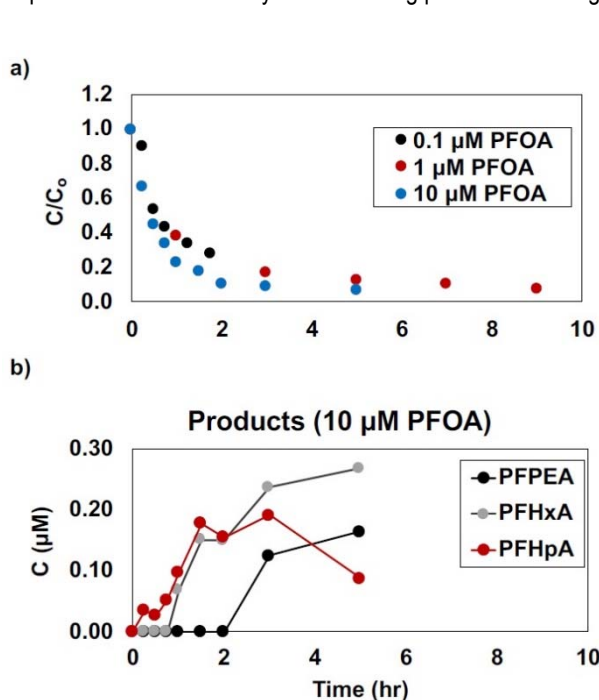


Figure 1 - (a) PFOA oxidation results, (b) product formation from 10 μM PFOA oxidation experiment.

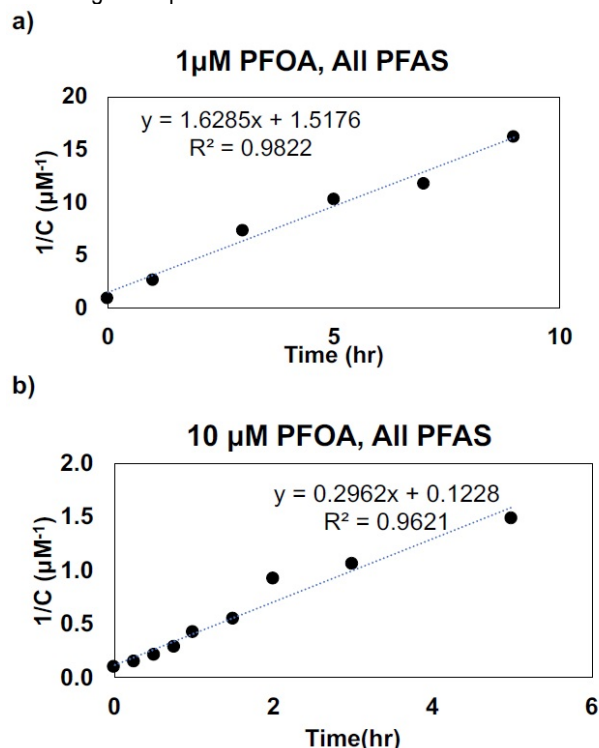


Figure 2 - Second-order kinetic modeling for total PFAS for initial PFOA concentration of (a) 1.0 μM and (b) 10 μM .

Kinetic modeling of the results is shown in Fig. 2 and indicates that the reactions are second-order with respect to total PFAS concentration. Only the 1.0 and 10 μM PFAS concentrations are shown because the 0.1 μM concentration had considerable noise in the data due to the very low product concentrations. The consequences of the second-order kinetics are that while high PFAS concentrations can be degraded very rapidly, low PFAS concentrations will require extended electrolysis times. These results suggest that PFAS oxidation should be coupled to an up-concentration step, which may be accomplished using sorbents or membranes. Future work will thus focus on evaluating this strategy and investigating the effect of REM properties to enhance PFAS reaction rates.

About the author



Dr. Brian P. Chaplin is Associate Professor in the Department of Chemical Engineering, at the University of Illinois at Chicago. He holds a B. Civil Engineering (1999) and an M.S. (2003) in Civil Engineering from the University of Minnesota and a Ph.D. in Environmental Engineering (2007) from the University of Illinois at Urbana-Champaign.